within the starch crystallites. The amorphous parts of starch thus would be expected to be less dense than the crystalline regions.

The dimensions of the unit cell of hydroxyethyl starch are quite similar to those of native starch except that the C_0 spacing is increased in hydroxyethyl starch to 9.7 Å in the highest substitution of 0.18 DS in corn starch. This increased the volume of the unit cell in hydroxyethyl starch (HES) by 4.3%. A width of 8 Å, or just half the 16 Å spacing, would be expected for the glucose unit in starch based on the periodicity of the starch helix in the starch-iodine complex which is 8 Å as stated by *Rundle* and *French* [12]. It is presumed that this corresponds to the width of the glucose residue. The thickness of the glucose residue appears to be about 4.5 Å in the carbohydrates in general, this is half the 9 Å spacing reported here. In the gross structure of starch, the planes of the glucose residues are probably parallel to the largest spacing of the cell. If adjacent glucose residues along the starch chain are identical in their configuration, the periodicity along the chain requires that adjacent glucose residues be rotated about b_0, so that the CH_2OH groups on adjacent glucose residues are trans to each other. These observations were based on the necessicity of displacing starch chains in opposite directions with respect to each other through the unit cell along b_0. This structure has been proposed on the basis of the unit cell dimensions and qualitative consideration of the intensities. From the above discussion it may be concluded that the induction of hydroxyethyl groups within starch chains increased the height of the unit cell. This increase may be due to the increase in volume of the substituted glucose residues which accommodate an arrangement free of strain. The increase in the volume of unit cell of substituted starch which was 4.3% in the 0.18 DS corn starch affords more uniform absorption of the dyes in starch coatings and sizings.

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Addresses of authors: Prof. Dr. *Saad Ibraheem El-Hinnawy*, Faculty of Agriculture, Ein Shams University; Asst. Prof. Dr. *Hani Mohamed El-Saied* and Prof. Dr. *Ahmed Effat El-Shirbeeny*, Faculty of Agriculture, Zagazig University; Dr. *Azeez Fahmy* and Dr. *Kamal Mahfouz El-Sahy*, Agriculture Research Centre (Egypt).

Storage Stability of Saponified Starch-g-Polyacrylonitrile and Related Absorbents*

By G. F. Fanta, E. B. Bagley, R. C. Burr and W. M. Doane, Peoria, Ill. (USA)

Use of methanol as a precipitant to isolate saponified starch-g-polyacrylonitrile from an aqueous alkaline saponification mixture gives a product with a higher water absorbency and better storage stability than that from precipitation with either ethanol, acetone, or isopropanol. Storage stability of the material is strongly dependent on moisture content of the polymer and is enhanced if excess alkali is neutralized before the product is isolated. Absorbent polymers prepared from flour suffer a greater absorbency loss on storage than starch-based polymers. Storage stabilities of drum dried-, freeze dried-, and tray dried products are also examined.

Lagerungsstabilität von verseiftem Stärke-g-Polyacrylnitril und verwandten Absorptionsmitteln. Die Verwendung von Methanol als Fällungsmittel zur Isolierung von verseiftem Stärke-g-Polyacrylnitril (Pfropfcopolymerisat aus Stärke und Polyacrylnitril) aus einer wäßrigen alkalischen Verseifungsmischung ergibt ein Produkt mit höherer Absorptionskapazität für Wasser und besserer Lagerungsstabilität als Produkte, die mit Ethanol, Aceton oder Isopropanol gefällt wurden. Die Lagerungsstabilität ist streng abhängig vom Feuchtigkeitsgehalt des Polymers und nimmt zu, wenn überschüssiges Alkali vor der Isolierung des Produktes neutralisiert wird. Aus Mehl hergestellte Absorptionspolymere zeigen bei der Lagerung größere Verminderungen der Absorptionsfähigkeit als Stärkepolymere. Die Lagerungsstabilitäten von trommel-, gefrier- und tellergetrockneten Produkten wurden ebenfalls geprüft.

1 Introduction

Acrylonitrile graft polymerizes readily onto starch with ceric ammonium nitrate initiation to yield starch-g-polyacrylonitrile (starch-g-PAN) containing about 50% by weight of grafted PAN (50% add-on) [1]. Saponification of starch-g-PAN with hot alkali converts the nitrile substituents of PAN to alkali metal carboxylate and carboxamide and yields a viscous dispersion of highly swollen but largely insoluble gel particles, which are apparently lightly crosslinked. Dewatering this dispersion can provide saponified (hydrolyzed) starch-g-PAN (HSPAN) in several different physical forms, depending on the dewatering or isolation technique used [2]. Alcohol precipitation is commonly used as an isolation method, but HSPAN can also be isolated by drum drying, freeze drying or tray drying to form thin, continuous films. Absorbent polymers have also been prepared by analogous procedures with flour instead of starch as a substrate for graft polymerization and with systems containing minor amounts of other monomers, such as 2-acrylamido-2-methylpropane-sulfonic acid (AASO$_3$H), in addition to acrylonitrile [3]. These absorbent polymers are being considered for a wide variety of industrial and agricultural applications. It was therefore of interest to determine how much of the original absorbency is lost through prolonged storage under different conditions, how storage stabilities compare among various absorbents, and how the stability of HSPAN varies with isolation conditions.

2 Experimental

2.1 Materials

Globe pearl corn starch (Globe 3005) was from CPC International and yellow corn flour was from Illinois Cereal Mills. Both products contained about 12% water. Acrylonitrile, Eastman practical grade, was distilled at atmospheric pressure through a 14-in. Vigreux column, and a center cut was collected. AASO$_3$H was from the Lubrizol Corp. and was used as received. Ceric ammonium nitrate was Fisher Certified ACS grade.

2.2 Synthesis of Graft Copolymers

A stirred slurry of 10.0 g (dry basis) of starch in 167 ml of water was heated at 85 °C for 30 min while a slow stream of nitrogen was bubbled through the mixture. The gelatinized starch slurry was cooled to 25 °C and 15.0 g of acrylonitrile was added, followed after about 30 s by a freshly prepared solution of 0.338 g of ceric ammonium nitrate in 3 ml of 1-N nitric acid. The mixture was stirred for 2 h at 25 °C (temperature controlled with ice-water) and then was neutralized to pH 6 − 7 with sodium hydroxide solution. Ethanol (200 ml) was added and the starch-g-PAN was removed by filtration. The polymer was washed with ethanol and dried under vacuum at 60 °C (yield: 24.5 g). Weight percent PAN in the graft copolymer (% add-on) was 59%, based on the weight gain of starch.

Starch-g-PAN from granular starch (55% add-on) was prepared in the same manner, except that the starch-water slurry was sparged with nitrogen for 1 h at 25 °C before polymerization.

Flour-g-PAN copolymers were prepared in the same way as starch graft copolymers. Granular and gelatinized corn flour gave graft copolymers with 40% and 53% add-on, respectively.

The same methods described for starch-g-PAN were used to prepare starch graft copolymers from 95:5 mole ratio mixtures of acrylonitrile (14.27 g) and AASO$_3$H (2.93 g). Granular and gelatinized starch graft copolymers had 56% and 57% add-on, respectively.

2.3 Saponification and Aging of Graft Copolymers

HSPAN Isolated by Precipitation

A suspension of 1.0 g of graft copolymer in 9 ml of 0.7-N sodium hydroxide solution was heated on a steambath for 5 − 10 min until the mixture thickened sufficiently to preclude settling. The flask was loosely stoppered (to permit escape of ammonia) and heated in a 95 − 100 °C oven for 3 h. The mixture was allowed to cool to room temperature and was then added to 350 ml of either methanol, ethanol, acetone or isopropanol in a Waring blendor. The mixture was stirred at high speed for 1 min, and the polymer was separated by filtration. The polymer was triturated in a mortar and pestle with about 30 ml of fresh organic solvent, let stand for 10 min and again separated by filtration.

In experiments with reduced amounts of methanol, the reaction mixture was blended with 35 ml of methanol. For the sample neutralized after precipitation, acetic acid was added dropwise, until a small amount of the precipitated solid gave a pH of 7.1 when it was dispersed in water. For the sample neutralized before precipitation, acetic acid was mixed into the reaction mass from saponification until a pH of 7.3 was reached, and the precipitation with 35 ml of methanol then was carried out. The polymer was separated by filtration and then was blended for 1 min with a fresh 35 ml portion of methanol. After the mixture was allowed to stand for 10 min, it was stirred for 30 s and the polymer was removed by filtration.

The solvent-wet polymer was separated into three portions, which were allowed to dry and age as follows:

(i) About ½ of the solvent-wet polymer was dried for about 18 h in a 60 °C vacuum oven (about 3 mm Hg). The polymer was ground to pass 60 mesh and the zero-time absorbency determined. The polymer then was divided into approximately equal portions. One portion was placed in a sealed screw-cap bottle, and the other was allowed to stand in an open bottle. Samples were allowed to age at 23 °C and 50% relative humidity.

(ii) About ¼ of the solvent-wet polymer was dried for about 18 h in a 60 °C forced air oven. The polymer was ground to pass 60 mesh, and the zero-time absorbency was determined. The polymer was placed in a sealed screw-cap bottle and allowed to age at 23 °C.

(iii) About ¼ of the solvent-wet polymer was allowed to air dry at 23 °C and 50% relative humidity. The polymer was ground to pass 60 mesh, and the zero-time absorbency was determined. The polymer was allowed to stand open to the atmosphere for three additional days. It was then placed in a sealed screw-cap bottle and allowed to age at 23 °C.

HSPAN Isolated by Drum, Tray, and Freeze Drying

A suspension of 3.0 g of starch-g-PAN (prepared from gelatinized starch) in 27 ml of 0.7-N sodium hydroxide solution was heated in a 95 − 100 °C oven for 3 h. The reaction mass was dispersed in about 700 ml of water and dialyzed against distilled water to remove excess alkali. The resulting dispersion (1168 g; pH 6.5) was divided into three approximately equal portions. The first portion was drum dried. Drums were heated with 40 psig steam and rotated at about 3 rpm. The

second portion was poured onto a Teflon-coated tray and dried to a film in a forced-air oven at 30–40°C (18 h). The third portion was freeze dried. Dry samples were allowed to age in sealed screw-cap bottles at 23°C.

2.4 Measurement of Water Absorbency

To determine water absorbency of dried, saponified polymers, an accurately weighed 1–5 mg sample of polymer (amount used depended on absorbency) was allowed to soak for 30 min in 50 ml of deionized water. The swollen polymer was then separated from unabsorbed water by screening through a tared 280 mesh sieve which was 4.8 cm in diameter. The polymer on the sieve was allowed to drain for 20 min, and the sieve was then weighed to determine the weight of water-swollen gel. Absorbency was calculated as grams of water per gram of polymer. No correction for moisture of the polymer was applied. Polymers with absorbencies over 1000 g/g had to be handled with extreme care to avoid break-up of the highly swollen particles and subsequent clogging of the sieve. Absorbencies were run in duplicate, and averages were recorded to two significant figures. Duplicate determinations agreed to within 10%.

3 Results and Discussion

3.1 Comparison of Precipitating Solvents

To determine whether the particular water-miscible organic solvent used to precipitate HSPAN from aqueous saponification reaction mixtures has an influence on the absorbency and storage stability of HSPAN, methanol, ethanol, acetone and isopropanol were compared as precipitants for HSPAN

prepared from gelatinized starch (Table 1). After each saponification, the aqueous alkaline reaction mass (about 10 g) was subjected to high-speed stirring with a large excess of organic solvent (350 ml). Precipitated HSPAN was then isolated by filtration, washed with fresh solvent and dried.

The solvent-wet polymer was divided into three portions, each of which was dried by a different method. The first portion was dried in a 60°C vacuum oven, while the second portion was dried in a 60°C forced-air oven. The third portion was simply allowed to air dry at 23°C and 50% relative humidity. Portions of each of these three samples were then placed in screw-capped bottles and allowed to stand at 23°C for periods of up to 1 year. At various time intervals, bottles were opened and small amounts of sample were removed for absorbency testing. To determine the effect of moisture absorption from the atmosphere on storage stability, a sample of HSPAN which had been dried under vacuum at 60°C was allowed to age at 23°C and 50% relative humidity in an unstoppered bottle.

It is apparent from Table 1 that the choice of precipitating solvent influences significantly the water absorbency of dry HSPAN; moreover, the observed decrease in absorbency in the series methanol, ethanol, acetone and isopropanol correlates with a decrease in dielectric constant of the solvent within this series. This correlation between absorbency and dielectric constant of the precipitating solvent is not unexpected. Since HSPAN is a polyelectrolyte, the maximum charge repulsion between macromolecular chains (and hence the maximum distance between these chains after the polymer has been precipitated and dewatered to form a rigid solid) will be in a solvent environment where the dielectric constant is high. When the dielectric constant of the medium is low, it is

Table 1.
Effect of Precipitating Solvent on Absorbency and Storage Stability[a].

Precipitating solvent	Dielectric Constant[b] 25°C	Aging Time, Days	60°C, Vac. Stoppered Bottle		60°C, Vac. Open Bottle		60°C, Forced Air Stoppered Bottle		Air Dry, 23°C Stoppered Bottle	
			Absorb. (g/g)	% Loss	Absorb. (g/g)	% Loss	Absorb. (g/g)	% Loss	Absorb. (g/g)	% Loss
Methanol	32.6	0	1700		1700		1900		1900	
		3	1700		1400	18	1800		1500	21
		17	1700		1400	18	1500		1400	26
		51	1700		1200	29	1600	16	1000	47
		181	1200	29	840	51	1100	42	660	65
		366	1100	35	630	63	1100		610	68
Ethanol	24.3	0	1300		1300		1000		720	
		3	1200		760	42	1000		600	17
		18	1100	15	530	59	790		500	31
		52	1100		520	60	870	13	460	36
		181	850	35	450	65	670		370	49
		364	780	40	370	72	680	32	350	51
Acetone	20.7	0	1100		1100		1100		810	
		3	1000		760	31	960		670	17
		18	1100		580	47	1000		590	27
		52	990	10	490	55	950	14	490	40
		182	820	25	420	62	770	30	420	48
		364	820		320	71	700	36	400	51
Isopropanol	18.3	0	920		920		890		680	
		3	910		730	21	880		570	16
		21	840	9	520	43	840		520	24
		54	820	11	400	57	750	16	410	40
		181	690	25	370	60	630		360	47
		364	680		280	70	670	25	340	50

[a] Saponified starch-g-PAN (HSPAN) prepared from gelatinized starch. One gram of starch-g-PAN saponified in 9 ml of 0.7-n NaOH. HSPAN precipitated with 350 ml of organic solvent. Samples stored at 23°C and 50% relative humidity.
[b] From CRC Handbook of Chemistry and Physics, 56th Ed., 1975–1976, p. E-56.

reasonable that individual polymer molecules would be in closer proximity to one another when precipitated. They can therefore more easily form hydrogen bonds or chemical crosslinks, either of which can lower the final water absorbency.

It is also apparent from Table 1 that the methods used to dry and store HSPAN will affect both water absorbency and the extent to which absorbency deteriorates with time. If oven-dried HSPAN is stored in a stoppered bottle so it cannot pick up atmospheric moisture, changes in absorbency are minimal during about the first 50 days of storage. There is then a slow decrease; and after 1 year, products have lost about 25 – 40% of their original absorbency. In an open bottle, however, the loss in absorbency is much more rapid. Presumably, moisture acquired from the atmosphere plasticizes HSPAN, and thus permits macromolecules to move in close enough proximity to each other to hydrogen bond or crosslink. In a study of soluble HSPAN, *Bagley* and *Taylor* [4] have also observed that crosslinking takes place more readily at high relative humidities, where polymers can absorb more atmospheric moisture. The air-dried sample will already have acquired some moisture from the atmosphere during the drying process, so it also loses absorbency rapidly, even though it is stored in a stoppered bottle.

The deterioration of water absorbency with time for vacuum oven-dried HSPAN samples precipitated with methanol, ethanol, acetone and isopropanol is shown in Figure 1 for samples aged in stoppered bottles, and in Figure 2 for samples aged while open to the atmosphere. In these figures, absorbency after a given number of days divided by the absorbency at time zero (A/A_0) is plotted against the logarithm of the storage time in days (log t). Time was plotted logarithmically to compress the total time scale and also to give an expanded scale at low values of t. It should be emphasized that the curves do not give information on actual absorbencies of HSPAN samples in g/g, but instead show what fraction of the original absorbency has been retained after a particular sample has been stored for a given period of time. Ranges in absorbency values between $t = 0$ and $t = 365$ days are given in figure legends, so actual absorbencies may be related to the plotted absorbency changes. Although different precipitating solvents give HSPAN samples with different absorbencies, Figure 1 shows that loss in absorbency with time is not greatly different for the four different princicipitants,
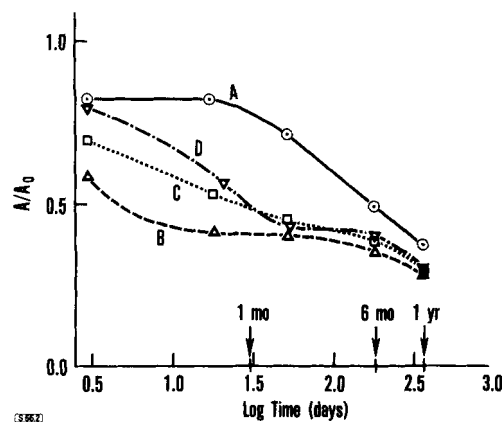

Figure 2. Same as Figure 1, except samples stored in bottles open to the atmosphere. (A) Methanol (1700 – 630 g/g); (B) Ethanol (1300 – 370 g/g); (C) Acetone (1100 – 320 g/g); (D) Isopropanol (920 – 280 g/g).

as long as samples are stored in stoppered bottles. When stored open to the atmosphere, however, the methanol-precipitated sample deteriorates less on standing than samples isolated by ethanol-, acetone- or isopropanol precipitation, especially in the first 4 – 5 months.

3.2 Methanol Precipitation: Comparison of Conditions

Since methanol precipitation gives higher absorbencies for HSPAN than the other solvents tested, we examined some variations in precipitation conditions with methanol to determine the effect on water absorbency and storage stability (Table 2). The amount of methanol used for the experiments in this table was reduced by a factor of 10, to more closely approximate a process which might be used commercially. Under the first set of conditions examined, HSPAN was isolated without neutralizing the excess alkali present in the product. These conditions are thus comparable to those of Table 1, except for the reduced amount of methanol. Under the second set of conditions in Table 2, the reaction mass from
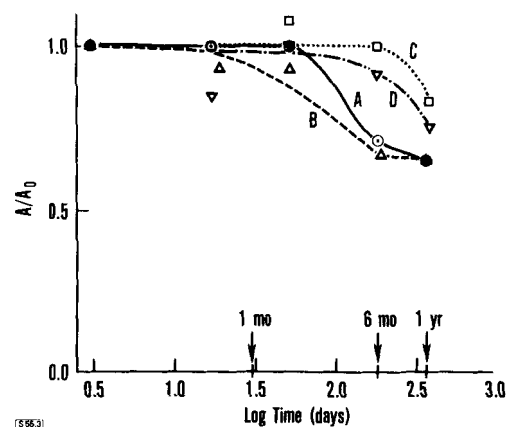

Figure 3. Absorbency loss of HSPAN samples stored in stoppered bottles. HSPAN prepared from gelatinized starch, precipitated with methanol, and dried in 60 °C vacuum oven. Comparison of precipitation conditions with methanol (1 g of starch-g-PAN saponified in 9 ml of 0.7-N NaOH; HSPAN precipitated with different volumes of methanol). (A) 350 ml, not neutralized (1700 – 1100 g/g); (B) 35 ml, not neutralized (1400 – 930 g/g); (C) 35 ml, neutralized after precip. (1200 – 1000 g/g); (D) 35 ml, neutralized before precip. (1100 – 830 g/g).
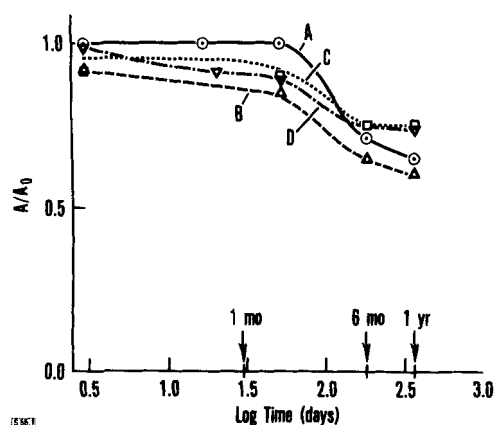
Figure 1. Absorbency loss of HSPAN samples stored in stoppered bottles. HSPAN prepared from gelatinized starch and dried in 60 °C vacuum oven. Comparison of solvents used for precipitation (1 g of starch-g-PAN saponified in 9 ml of 0.7-N NaOH; HSPAN precipitated with 350 ml of organic solvent). (A) Methanol (1700 – 1100 g/g); (B) Ethanol (1300 – 780 g/g); (C) Acetone (1100 – 820 g/g); (D) Isopropanol (920 – 680 g/g).

Table 2.
Precipitation with Reduced Amounts of Methanol[a]. Effect of Precipitation Conditions.

Conditions	Aging Time (Days)	60°C, Vac., Stoppered Bottle		60°C, Vac., Open Bottle		60°C, Forced Air, Stoppered Bottle		Air Dry, 23°C, Stoppered Bottle	
		Absorb. (g/g)	% Loss	Absorb. (g/g)	% Loss	Absorb. (g/g)	% Loss	Absorb. (g/g)	% Loss
Not Neutralized	0	1400		1400		1300		1500	
	3	1400		1300		1400		1400	
	19	1300		980	30	1200		1200	20
	52	1300		930	34	1300		1000	33
	194	940	33	650	54	930	28	680	55
	363	930		490	65	860	34	590	61
Neutralized before Precipitation	0	1100		1100					
	17	930		810	26				
	52	1100		850					
	181	1000	9	610	45				
	379	830	25	430	61				
Neutralized after Precipitation	0	1200		1200					
	17	1200		1100					
	52	1300		1000	17				
	181	1200		740	38				
	379	1000	17	490	59				

[a] Saponified starch-g-PAN (HSPAN) prepared from gelatinized starch. One gram of starch-g-PAN saponified in 9 ml of 0.7-N NaOH. HSPAN precipitated with 35 ml of methanol.

saponification was neutralized with acetic acid before HSPAN was precipitated. In the final series, excess alkali was neutralized with acetic acid after the reaction mass was blended with methanol to precipitate HSPAN.

If these results are compared with those of Table 1, it is apparent that a tenfold reduction in the amount of methanol precipitant reduces the absorbency of HSPAN by a small but significant amount. Additional reductions in absorbency are observed when the excess alkali in HSPAN is neutralized with acetic acid before products are isolated. Plots of storage stability (A/A_0) in stoppered bottles vs. log t (Fig. 3) show that the two neutralized samples are more stable than those which are isolated without neutralization, even though the initial absorbencies are lower (methanol data from Table 1 has also been plotted in this figure for comparison). When samples are stored open to the atmosphere, however, absorbency losses are appreciable; and large differences between individual samples are not seen (Fig. 4).
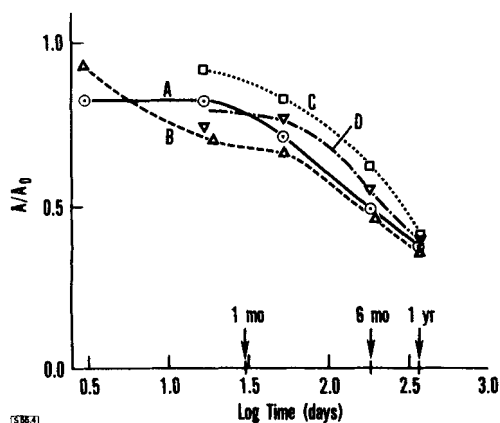

Figure 4. Same as Figure 3, except samples stored in bottles open to the atmosphere. (A) 350 ml, not neutralized (1700 − 630 g/g); (B) 35 ml, not neutralized (1400 − 490 g/g); (C) 35 ml, neutralized after precip. (1200 − 490 g/g); (D) 35 ml. neutralized before precip. (1100 − 430 g/g).

3.3 Comparison of Starch, Flour and Comonomer Absorbents

Although our research with absorbent polymers has dealt mainly with those prepared by graft polymerization of acrylonitrile onto gelatinized starch, there are some closely related graft copolymers which also give useful absorbents when saponified with aqueous alkali [3]. For example, either granular starch, granular flour or gelatinized flour may be substituted for gelatinized starch in the graft polymerization reaction. Also, either granular or gelatinized starch may be graft polymerized with mixed monomer systems that contain largely acrylonitrile with minor amounts of a comonomer, such as $AASO_3H$. The water absorbency of these various polymers and the dependence of absorbency on polymer structure has been studied in detail [3].

To determine whether certain graft copolymer absorbents might exhibit greater storage stability than others, granular starch-g-PAN, granular and gelatinized flour-g-PAN, and granular and gelatinized starch-g-poly(acrylonitrile-co-$AASO_3H$) were saponified, precipitated with methanol and dried under the conditions described for Table 1. Storage stability data is presented in Table 3, and plots of A/A_0 vs. log t for 60°C vacuum-dried samples are shown in Figure 5 for storage in stoppered bottles, and in Figure 6 for storage in bottles open to the atmosphere. Curves for the gelatinized starch-g-PAN absorbent are taken from Figures 1 and 2.

Although granular starch-based products have lower absorbencies in g/g than the corresponding products from gelatinized starch, it is apparent from Figure 5 that the absorbents prepared from granular starch show a negligible deterioration on prolonged storage in stoppered bottles. Since saponification does not disrupt the granular appearance of starch-g-PAN [5], it is possible that granular starch-based HSPAN has a more structured matrix than that prepared from gelatinized starch and the polymer chains thus have restricted mobility. The association of individual macromolecules due to collapse of swollen gel particles during dewatering might therefore be inhibited. The reduced

Table 3.
Storage Stability of Starch and Flour-Based Absorbents[a].

Polymer Saponified	Aging Time (Days)	60°C, Vac., Stoppered Bottle		60°C, Vac., Open Bottle		60°C, Forced Air, Stoppered Bottle		Air Dry, 23°C, Stoppered Bottle	
		Absorb. (g/g)	% Loss	Absorb. (g/g)	% Loss	Absorb. (g/g)	% Loss	Absorb. (g/g)	% Loss
Granular Starch-g-PAN	0	260		260		220		220	
	3	240		230		260		220	
	19	270		240		280		240	
	53	240	8	190	27	220		180	
	186	220		190		260		210	
	364	240		180	31	230		200	9
Granular Flour-g-PAN	0	1300		1300		1100		1100	
	3	1100	15	920	29	1000		910	17
	17	810		560	57	790		680	38
	52	1100		420	68	890	19	560	49
	182	820	37	180	86	780	29	400	64
	365	870		140	89	840		410	
Gelatinized Flour-g-PAN	0	2500		2500		1800		3000	
	3	2400		1600	36	2100		1800	40
	17	2100	16	1300	48	2200		1200	60
	52	1700	32	660	74	1600	11	860	71
	181	1400	44	230	91	1500	17	590	80
	365	1400		200	92	1400	22	470	84
Granular Starch-g-poly(acrylonitrile-co-AASO₃H)	0	690		690		650		630	
	3	640		490		570		540	
	18	690		480		640		550	
	54	720		500	28	700		570	10
	182	580	16	410	41	510	22	450	29
	362	630		280	59	510		430	32
Gelatinized Starch-g-poly(acrylonitrile-co-AASO₃H)	0	2800		2800		2100		2100	
	3	2800		2600		2300		2000	
	17	2600		1400	50	2500		1700	19
	52	3000		1100	61	2400		1200	43
	182	1800	36	670	76	1400	33	770	63
	364	1900		330	88	1700		660	69

[a] One gram of graft copolymer saponified in 9 ml of 0.7-N NaOH. Polymer precipitated with 350 ml of methanol.
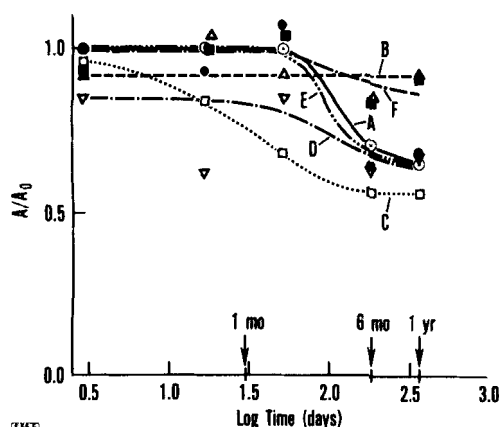

Figure 5. Absorbency loss of different absorbent polymers stored in stoppered bottles. One gram of graft copolymer saponified in 9 ml of 0.7-N NaOH. Polymer precipitated with 350 ml of methanol and dried in 60°C vacuum oven. (A) Gelat. Starch-g-PAN (1700 – 1100 g/g); (B) Gran. Starch-g-PAN (260 – 240 g/g); (C) Gelat. Flour-g-PAN (2500 – 1400 g/g); (D) Gran. Flour-g-PAN (1300 – 870 g/g); (E) Gelat. Starch-g-poly(acrylonitrile-co-AASO₃H) (2800 – 1900 g/g); (F) Gran. Starch-g-poly(acrylonitrile-co-AASO₃H) (690 – 630 g/g).
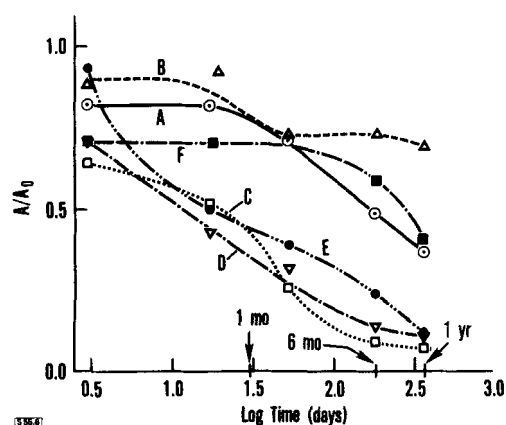

Figure 6. Same as Figure 5, except samples stored in bottles open to the atmosphere. (A) Gelat. Starch-g-PAN (1700 – 630g/g); (B) Gran. Starch-g-PAN (260 – 180 g/g); (C) Gelat. Flour-g-PAN (2500 – 200 g/g); (D) Gran. Flour-g-PAN (1300 – 140 g/g); (E) Gelat. Starch-g-poly (acrylonitrile-co-AASO₃H) (2800 – 330 g/g); (F) Gran. Starch-g-poly(acrylonitrile-co-AASO₃H) (690 – 280 g/g).

amount of water-soluble HSPAN (as opposed to gel) produced during aqueous saponification of a granular starch-

based product, as compared with a product derived from gelatinized starch [6], might also be a factor in the amount of association that takes place during precipitation. As opposed to the starch-based absorbents, the product derived from granular flour-g-PAN loses a large percentage of its absorbency on standing. Denaturation of the protein component of flour might be one reason for this observation.

When samples are stored in bottles open to the atmosphere (Figure 6), absorbencies decrease much more rapidly than they do in stoppered bottles; however, the granular starch-based products are still more stable than their gelatinized counterparts. The granular and gelatinized flour-based products suffer the greatest deterioration in absorbency; about 90% of their original absorbencies are lost after storage for 1 year.

3.4 Stability of HSPAN Isolated by Drum, Tray and Freeze Drying

Although HSPAN is commonly isolated from water dispersion by precipitation with a water-miscible non-solvent, other methods of product isolation may also be used to obtain HSPAN in a variety of physical forms [2]. Drum drying a water dispersion of HSPAN followed by coarse grinding provides the absorbent polymer in flake form, whereas freeze drying affords the polymer in the form of a soft, spongy pad. Finally, if the water dispersion is spread onto a tray and allowed to dry at room temperature, a continuous film of HSPAN is obtained.

Since any one of these forms might find use for a specific application, we studied the storage stability of drum-dried, freeze-dried, and tray-dried HSPAN in stoppered bottles (Table 4 and Fig. 7). The three samples were prepared from gelatinized starch, and samples were purified by dialysis before product isolation. All three samples lost absorbency with prolonged storage; however, the percentage of the original absorbency lost was least with the drum dried sample. Absorbency loss was greatest with freeze dried HSPAN.

Table 4.
Stability of Saponified Starch-g-PAN[a] Isolated by Drum-, Tray-, and Freeze Drying.

Drum Drying[b]			Freeze Drying			Tray Drying (Film)[c]		
Aging Time (Days)	Absorb. (g/g)	% Loss	Aging Time (Days)	Absorb. (g/g)	% Loss	Aging Time (Days)	Absorb. (g/g)	% Loss
0	370		0	650		0	680	
20	360		20	490	25	20	710	
51	350		53	340	48	51	560	18
182	280	24	182	250	62	182	360	47
365	250	32	364	210	68	365	330	51

[a] Saponified starch-g-PAN (HSPAN) prepared from gelatinized starch. Three grams of starch-g-PAN saponified in 27 ml of 0.7-N NaOH. HSPAN purified by dialysis before drying.
[b] Drums heated with 40 psig steam and rotated at about 3 rpm.
[c] Dried in forced air oven at 30–40°C (18 h).

The low initial absorbency value of 370 g/g for the drum-dried sample can be explained by association and crosslinking between macromolecules caused by the high temperature and high moisture conditions encountered during the drying process. Since interactions between polymer chains have already been maximized, further association, with the
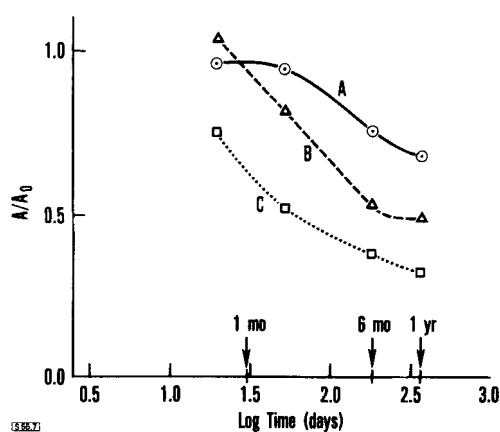

Figure 7. Absorbency loss of drum dried-, tray dried-, and freeze dried HSPAN prepared from gelatinized starch. Samples stored in stoppered bottles. (A) Drum dried (370–250 g/g); (B) Tray dried (680–330 g/g); (C) Freeze dried (650–210 g/g).

accompanying loss of absorbency, is minimal. In other words, if we refer to a plot of A/A_0 vs. log t, a drum-dried sample is starting out at time zero where a typical precipitated sample has begun to level off.

The rapid loss of absorbency of the freeze-dried sample was at first unexpected, since one might assume that freezing would lock the swollen gel structure into a configuration where separation of macromolecular chains would be at a maximum as water is being evaporated. This, however, is not what takes place [7]. In hydrated biopolymers, supercooling occurs; and once ice crystals begin to form, water from nearby areas diffuses into growing crystals. A significant amount of water, however, remains bound to the polymer, and this water does not freeze, even at low temperatures. Molecules of HSPAN thus remain plasticized with water during the drying process; and in this respect, freeze drying and tray drying are analogous. The formation of ice crystals could also force the HSPAN polymer into configurations which maximize polymer-polymer interactions.

4 Conclusions

To achieve maximum water absorbency, methanol is the solvent of choice for precipitating HSPAN from water dispersion; traces of alkali present in the precipitated product should be neutralized before the polymer is isolated and dried. Although the water absorbency decreases if HSPAN is allowed to absorb moisture from the atmosphere, the polymer is stable for an extended time period if it is kept in a sealed container. The absorbency decrease observed for products stored for prolonged periods of time in stoppered bottles is probably due to a minor amount of atmospheric moisture acquired when samples were ground after drying and when bottles were periodically opened to the atmosphere to remove small quantities of material for absorbency testing. A storage-stable HSPAN polymer can thus be prepared with the proper control of process variables and the control of moisture in the stored material. Moreover, if a somewhat lower absorbency is desired (for example, to promote faster wicking of water into the absorbent and thus to minimize the gumballing phenomenon) this result can also be achieved by simply storing HSPAN under conditions of high relative humidity. Variations in storage conditions therefore constitute one more method by which the properties of HSPAN may be tailored to fit specific applications.

Summary

Use of methanol as a precipitant to isolate saponified starch-g-polyacrylonitrile (HSPAN) from an aqueous alkaline saponification mixture gives a product with a higher water absorbency and better storage stability than that resulting from precipitation with either ethanol, acetone, or isopropanol. Storage stability of HSPAN samples is strongly dependent on moisture content of the polymer. If HSPAN is allowed to absorb atmospheric moisture, water absorbency of the polymer decreases more rapidly on storage than if the same polymer is stored in a sealed container. Storage stability is enhanced if excess alkali in the saponification mixture is neutralized before the product is isolated. Although absorbent polymers prepared from granular starch have lower absorbencies than comparable products prepared from gelatinized starch, granular starch-based polymers lose a smaller percentage of their original absorbency on storage. Absorbent polymers prepared from flour suffer a greater absorbency loss on storage than starch-based polymers. Storage stabilities of drum dried-, freeze dried-, and tray dried-HSPAN are also examined.

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Address of authors: Dr. *G. F. Fanta*, Dr. *E. B. Bagley*, Mr. *R. C. Burr* and Dr. *W. M. Doane*, Northern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, Peoria, Illinois 61604 (USA).

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